

Folding Langmuir Monolayers

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The maximum pressure a two-dimensional surfactant monolayer is able to withstand is limited by the collapse instability towards formation of three-dimensional material. We propose a new description for reversible collapse based on a mathematical analogy between the formation of folds in surfactant monolayers and the formation of Griffith Cracks in solid plates under stress. The description, which is tested in a combined microscopy and rheology study of the collapse of a single-phase Langmuir monolayer of 2-hydroxy-tetracosanoic acid (2-OH TCA), provides a connection between the in-plane rheology of LM's and reversible folding.

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The collapse of deformable structures under stress has fascinated scientists and engineers since 1744 when Euler presented his linear stability analysis of the large-scale structural failure of plates, known as the *buckling instability* [1]. In the physics literature, recent research in this area has focused on the local structure of crumpled surfaces [2] and on the geometry of the fold lines [3]. Langmuir monolayers (LM's), insoluble surfactant films resting on an air-water interface, constitute a natural arena for the study of the collapse of surfaces at the molecular level. LM's are stable at low surface pressures π , but collapse into the third dimension when sufficiently compressed. While collapse can occur by the nucleation and growth of the bulk phase, Euler-type buckling phenomena are well documented [4]. Linear stability analysis [5] shows that when the surface tension $\gamma = \gamma_w - \pi$ of a LM vanishes (with $\gamma_w \approx 72$ mN/m the surface tension of water), the air-water interface indeed should become unstable against mechanical buckling. However, the collapse of LM's exhibiting buckling-type phenomena actually takes place for *positive* surface tensions γ in the range of 1-10 mN/m, which casts doubt on Euler buckling as the underlying mechanism. The introduction of spontaneous curvature into the free energy of the film does lower the instability threshold, but only by a small amount [6].

Recent experimental studies demonstrated that certain of these LM's undergo *reversible* collapse, i.e., with little or no hysteresis in the pressure-area isotherms. Although this was first seen under conditions where there is

coexistence in the LM between an isotropic liquid phase and islands of a condensed phase [7,8] it has also been observed for a one-component monophasic material [9]. During reversible collapse, large isolated folds into the subphase appear at the collapse point; they remain fully connected to the monolayer and open reversibly when the film is re-expanded. There is special interest in reversible folding because of the recent proposal [10] that it plays an essential role in the functioning of lung surfactant.

The aim of this letter is to propose that reversible collapse in LM's is unrelated to the (linear) Euler instability but instead to a general, non-linear instability of *deformable surfaces with self-attraction*. This instability is closely related to a classical problem in structural failure of plates under stress, namely crack formation. The "mapping" between the two problems can be tested experimentally and provides a scenario for reversible fold formation in terms of the in-plane rheology of LM's.

The mechanism is shown in Fig. 1a. Assume a rectangular, self-adhering elastic sheet of thickness d with a two-dimensional (2D) shear modulus G , an area modulus K , a bending modulus κ and a self-adhesion energy per unit area W . For LM's consisting of long-tailed surfactant molecules, $W/2$ can be identified as the free energy cost of creating a unit area of hydrocarbon surface exposed to air, i.e., with the *surface energy* γ_H of a hydrocarbon fluid (for a wide range of hydrocarbons γ_H lies in the limited range of 25 ± 4 mN/m [11]).

Let this sheet be stretched along the y direction by a traction force per unit length γ with the sheet width along the x direction kept fixed. Now create a bilayer fold of length L along the x direction, with a fold profile $U(x)$. This means that the y-component of the in-plane elastic displacement field undergoes a mathematical discontinuity $\pm U(x)$ along the fold line. Let σ_{ij} be the contribution to the elastic stress tensor introduced by the fold, so $\sigma_{ij} = 0$ far from the fold. Under quasi-static conditions, the elastic force per unit length $\gamma + \sigma_{yy}(x)$ pulling material out of the fold should equal the force per unit length $W/2$ pulling material into the fold. Hence, $\sigma_{yy}(x)$ must be a constant along the fold line equal to $W/2 - \gamma$.

These unusual boundary conditions on the stress tensor have the same mathematical form as those encountered in the materials-science problem of the formation of

cracks in plates under an external traction force per unit area P , known as *Griffith Cracks* (GC). Traction-induced crack formation of plates can be considered as the analogue of adhesion-induced fold formation of a LM, albeit with the sign of the displacement field and the stresses reversed. For a GC, the boundary condition along the crack surface states that the total stress must vanish along the crack so $\sigma_{yy} = -P$. By replacing P with $\gamma - W/2$ in the corresponding expressions for a Griffith Crack [1] we obtain the following prediction for the shape of a fold in a solid LM:

$$U(x)/L = \frac{[W/2 - \gamma]}{Y} \sqrt{1 - (2x/L)^2} \quad (1)$$

with $Y = 4KG/(K + G)$ the (two-dimensional) Young's Modulus. Folds in solid LM's thus should have a *semi-elliptical* shape with a ratio $\Gamma = U(0)/L$ between short and long axes that should be a fold-independent material parameter. According to Eq. 1, fold formation indeed can start for positive surface tensions γ , i.e. when the surface tension γ drops below $W/2$, which corresponds to surface pressures exceeding $\gamma_w - \gamma_H = 53 \pm 4$ mN/m.

To test the proposed mapping, we examined folding in a relatively simple system that involves only a single component and a single monolayer phase. The collapse of 2-hydroxytetracosanoic acid (2-OH TCA) is characterized by the reversible appearance and growth of large folds projecting into the subphase [9]. Folds can be observed by light-scattering microscopy (LSM) – which is sensitive to height differences – with the resulting images providing a projection of the fold on the air-water interface. As shown in Fig. 1b, the shape of folds near onset indeed can be fitted to a semi-ellipse. The growth of a number of folds upon area reduction was recorded on videotape, with the simultaneous changes in the fold width $U(0)$ and the fold length L , obtained from a fit of the fold to a semi-ellipse, determined by a frame-by-frame analysis of the images. Figure 2 shows $U(0)$ vs. L for three representative folds. As predicted, $U(0)$ depends linearly on L for each of the folds and the slopes Γ are essentially identical, 0.25 ± 0.5 . The intercepts are zero within the (limited) precision of the data.

In order to compare the measured values of Γ and that predicted by Eq. 1, we studied the rheological properties of 2-OH TC. From the pressure-area isotherm, we obtained an area compression modulus of 610 ± 10 mN/m near the collapse pressure. Using a Couette viscometer, designed for rheology studies of LM's [12], we measured the frequency-dependent complex shear modulus $G^*(\omega)$ near the collapse pressure over a frequency range of 0.001 to 0.1 Hz. As shown in Fig. 3, the real (elastic) part $G'(\omega)$ of the shear modulus varies between 0.4 and 7 mN/m over this frequency range, while the imaginary (dissipative) part $G''(\omega)$ varies between 1.6 to 16 mN/m. In another experiment the relaxation of shear stress was monitored by rotating the outer cylinder with

a constant rate of strain of 0.005 s^{-1} for 30 s while monitoring the stress on the inner cylinder. The outer cylinder was suddenly stopped, and the stress on the inner cylinder was measured for an additional 30 s. The resulting stress relaxation could be fitted by a single relaxation time $\tau_s = (24 \pm 2) \text{ s}$. These results indicate that 2-OH TCA has to be considered as a 2D viscoelastic material, probably due to a significant area concentration of 2D structural defects such as grain boundaries.

In order to describe fold formation in a self-adhering viscoelastic sheet, we continued to use Eq. 1 but simply replaced the shear modulus G by $|G^*(\omega_t)|$ with $t = 2\pi/\omega_t$ the age of the fold. For a Maxwellian viscoelastic material, with a single stress relaxation time τ_s , this procedure reproduces Eq. 1 in the short time limit while in the long time limit it leads to a semi-elliptical *flow profile* $V(X) \approx U(X)/\tau_s$, consistent with fold formation in a self-adhering 2D fluid sheet having a surface viscosity $\eta = G\tau_s$. Using Fig. 3 to estimate $|G^*(\omega_t)|$, with t of the order of 10^2 s, together with our earlier result $W/2 - \gamma = 13 \pm 2$ mN/m, we obtain for Γ a value of the order of 0.6. This is in rather reasonable agreement with the observed range but a precise comparison clearly requires a consistent description of fold growth in self-adhering viscoelastic sheets.

If we accept the mapping between LM folds and GC's, then we can use the extensive literature on GC's to describe the formation of reversible folds. For a GC, the stress field diverges near the crack endpoints as $1/r^{1/2}$, and the divergence of the stress leads to a zone of plastic deformation or fracture near the endpoints. For viscoelastic LM's, we must expect similar plastic high stress zones at the endpoints, except that the film may be buckled out of the plane in order to reduce this stress. The stress divergence near GC endpoints produces a "crack-widening force" $f(L) = \epsilon L$ proportional to the crack length L [1], which should be present as well for folds. We indeed observed a steady lateral widening of the giant folds when we reduced the LM area. This fold-widening force, is counteracted by the fold *line tension* τ , due the highly curved edge that borders the fold (see Fig. 1A). Within the Helfrich description of LM's [13], the fold line tension τ is related to the LM bending energy κ and the film thickness d by $\pi\kappa/2d$. Measurements of the bending modulus κ by diffuse x-ray scattering [14] on LM's with tail lengths similar to 2-OH TCA lead to values for κ in the range of 200 - 500 $k_B T$.

Because of the competition between the two forces, a fold with $L > \tau/\epsilon$ will grow spontaneously while for $L < \tau/\epsilon$ a fold will shrink. The critical fold length $L^* = \tau/\epsilon$ and the nucleation energy barrier $\Delta E = 1/2\tau L^*$ can be obtained from the corresponding expressions for GC's [1]:

$$L^* = \frac{2}{\pi} \frac{\tau Y}{(W/2 - \gamma)^2} \quad (2)$$

The parameters entering Eq. 2 are experimentally acces-

sible. For a viscoelastic LM we replace G by $|G^*(\omega_f)|$ with $2\pi/\omega_f$ the formation time of the fold (of the order of seconds or faster).

Because the nucleation barrier diverges at $W/2$ equal to γ , Eq. 2 explains why the collapse of 2-OH TCA required significantly higher pressures than the nominal onset value $\gamma_w - \gamma_H = 53 \pm 4$ mN/m as predicted by Eq. 1. Next, since formation times are short compared to the stress relaxation time, $|G^*(\omega_f)|$ is of the order of 100 nN/m or higher. Equation 2 then predicts that the critical fold length L^* should be in the range of 100 Å or longer and that the nucleation energy barrier ΔE should be in the range of 20 k_BT or higher. It follows that *fold formation in solid or viscoelastic LM's cannot proceed spontaneously but requires the presence of large, pre-existing structural defects*. We were not able to identify the nature of these defects with LSM. Diamant et al. [15] proposed that for multi-component LM's, phase boundaries would be natural sites for the nucleation of folds (due to differences in spontaneous curvature between phases). This explanation cannot hold for monophasic materials, like 2-OH TCA, but buckling along grain boundaries may play a similar role.

We conclude by noting that, according to Eq. 2, out-of-plane reversible folding should be sensitively dependent on the in-plane rheological properties of the LM. If fold formation is desirable, as in the case of lung surfactant, than this could be achieved with additives such as cholesterol that increase the fluidity of a surfactant layer, and hence reduce $|G^*(\omega_f)|$ without affecting the structural integrity of the film.

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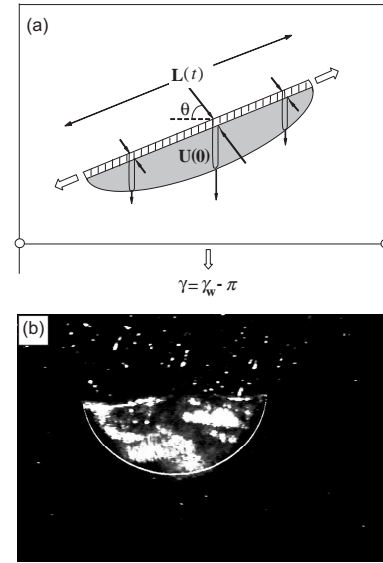


FIG. 1. (a) Schematic diagram of a fold showing the position-dependent fold width $U(x)$ and the fold length L . (b) Light scattering microscope image of an early giant fold in 2-OH TCA. Its length is 65 μm . The fold is bent in a nearly horizontal plane beneath the monolayer. The line is a semi-ellipse fitted to the fold profile.

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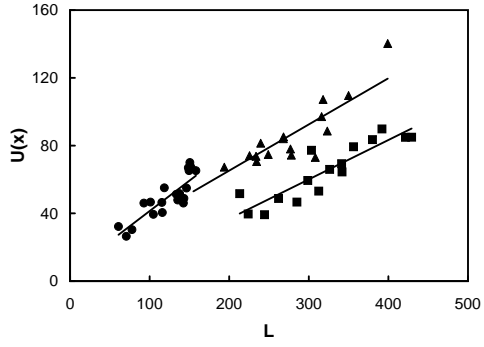


FIG. 2. $U(x=0)$ vs. L for three folds. The data were obtained from a frame-by-frame analysis of videotapes of during fold widening under compression and are given in numbers of pixels.

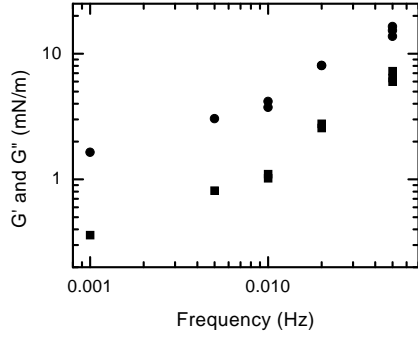


FIG. 3. Values of G' (lower line) and G'' (upper line) in mN/m as a function of the oscillation frequency for 2-OH TCA at 20 °C at a pressure of 60 mN/m.